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<p>(30) Priority: October 9, 1985, Germany 3535985  (43) Publication Date of Patent Granting: May 13, 1987, Patent Bulletin 87/20  (84) Designated Countries: DE FR GB IT</p>	<p>(71) Applicant: BAYER AG Konzernverwaltung RP Patentabteilung D-5090 Leverkusen 1 Bayerwerk, Germany  (72) Inventor: Zabrocki, Karl, Dr. Edelfalter 33 D4044 Büttgen, Germany  (72) Inventor: Reinking, Klaus, Dr. Robert-Stolz-Strasse 16 b D-5632 Wermelskirchen, Germany  (72) Inventor: Köhler, Karl-Heinz, Dr. Buschstrasse 165 D4150 Krefeld, Germany  (72) Inventor: Lange, Ralf, Dr. Bethelstrasse 19 D-4150 Krefeld 1, Germany</p>
<p>(54) Mineral-filled thermoplastic polyesters, techniques for their production, and their use as molding materials.</p> <p>(57) By the addition of ground quartz and/or ground cristobalite to thermoplastic polyesters, mixtures can be obtained, which possess the typical benefits of mineral-filled polyesters, without a loss of tenacity [toughness] occurring.</p>	

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Mineral-filled thermoplastic polyesters, techniques for their production, and their use as molding materials

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The invention concerns thermoplastic processable polyesters that contain ground quartz and/or ground cristobalite as filling materials, a technique for their production, and their use as molding materials, primarily for injection molding.

With non-fiber-forming minerals, filled thermoplastic polyesters have been used as materials in the fields of electro-technology and electronics as well as in the construction of vehicles for the production of the most diverse shaped parts. The main advantages of such materials are their high chemical and thermal resistance as well as the easy workability, e.g., in the injection molding technique.

Compared with unreinforced and fiber-forming inorganic filling materials, e.g., glass fibers, the polyesters formed as mineral-filled polyesters are characterized by an enhanced surface gloss, high leakage and light-arc stability, as well as low delay [sic] upon solidifying the shaped part.

When fiber-forming mineral filling materials had not come into use, different materials were used, for example, talc (DE-OS 20 51 331, 20 51 333), dolomite (EP-A 57,161), novaculite (US-PS 37 40 341, 37 45 140, 40 18 738), kaolin, mica, alumina, and silica gel (JP-PS 15 191/69).

The disadvantage of the tenacity loss counteracts the benefits offered by mineral-filled polyesters. By the use of as good as possible filling materials, can one try to keep this disadvantage to a minimum; completely avoiding it has however not yet been possible.

In US-PS 37 40 371, it is stated why novaculite-containing filled polyesters have better mechanical characteristics than polyesters filled with other minerals: first of all, the hydrophilic

surface permits a more solid bond between the filling material and the polyester; secondly, tension-tapering to the boundary area is avoided in the filling material/polyesters due to the absence of sharp edges with cryptocrystalline novaculite. However, this is important particularly with respect to the brittle nature of partly crystalline polyesters.

It was now surprisingly found that one could obtain polyesters that possess the benefits of mineral-filled polyesters, without a tenacity loss, if one used ground quartz more and/or ground cristobalite, whose particle diameter does not exceed a certain value, as filling material.

The subject of the invention thus concerns mixtures made from:

- A) 20 to 80 wt%, preferably 40 to 75 wt%, of a thermoplastic polyester,
- B) 5 to 50 wt%, preferably 20 to 50 wt%, of a mineral filling material,
- C) 0 to 30 wt%, preferably 0 or 10 to 25 wt%, of an acrylate or butadiene rubber,
- D) 0 to 30 wt% of glass fibers, and
- E) 0 to 10 wt% of ordinary auxiliary materials,

whereby the percentage figures refer to the sum of components A to E,

thus characterized by the fact that the filling material B is ground quartz and/or ground cristobalite, for which at least 50 wt% possess a particle diameter of 2.5  $\mu\text{m}$  at the most.

Thermoplastic polyesters A in the sense of the invention are reaction products of aromatic dicarboxylic acids or their reactive derivatives (for example, dimethyl esters or anhydrides) and aliphatic, cyclo-aliphatic, araliphatic, or aromatic diols.

Preferential polyesters A are produced from terephthalic acid (or their reactive derivatives) and alkane diols with 2 to 10 C atoms according to well-known methods (synthetic manual, Vol. VIII, p. 695 ff, Carl Hanser Verlag, Munich, 1973).

Preferably, polyalkylene terephthalate A contains at least 80, preferably at least 90 mol%, in relation to the dicarboxylic acid component, of terephthalic acid residues and at least 80, preferably at least 90 mol%, in relation to the diol components, of ethylene glycol and/or 1,4-butanediol residues.

The preferential polyalkylene terephthalate A, besides terephthalic acid esters, can contain up to 20 mol% of residues of other aromatic or cyclo-aliphatic dicarboxylic acids with 8 to 14 C atoms and/or aliphatic dicarboxylic acids with 4 to 12 C atoms, e.g., residues of phthalic acid, isophthalic acid, naphthalene-2,6-dicarboxylic acid, diphenyl-4,4'-dicarboxylic acid, succinic acid, sebacic acid, or cyclohexane diacetic acid.

The preferential polyalkylene terephthalate A, besides ethylene glycol and/or 1,4-butanediol residues, can contain up to 20 mol% of other aliphatic diols with 3 to 21 C atoms or cyclo-aliphatic diols with 6 to 21 C atoms, e.g., residues of 1,3-propanediol, 2-ethyl-1,3-propanediol, neopentyl glycol, 1,5-pentandiol, 1,6-hexanediol, 1,4-cyclohexanedimethanol, 3-methyl-2,4-pentanediol, 2-methyl-2,4-pentanediol, 2,2,4-trimethyl-1,3-pentanediol, 2,2,4-trimethyl-1,5-pentanediol, 2-ethyl-1,3-hexanediol, 2,5-diethyl-1,3-propanediol, 2,5-hexanediol, 1,4-di-( $\beta$ -hydroxyethoxy)-benzene, 2,2-bis(4-hydroxycyclohexyl)-propane, 2,4-dihydroxy-1,1,3,3-tetramethylcyclobutane, 2,2-bis(3- $\beta$ -hydroxyethoxyphenyl)-propane, and 2,2-bis(4-hydroxypropoxyphenyl)-propane (DE-OS 24 07 674, 24 07 776, and 27 15 932).

The polyalkylene terephthalate A can be branched by the insertion of relatively small amounts of trivalent or tetravalent alcohols or trivalent or tetravalent carboxylic acids, as they are described, e.g., in DE-OS 19 00 270 and US-PS 36 92 744. Examples of preferential ramifying agents are trimesic acid, trimellitic acid, trimethylolethane, trimethylolpropane, and pentaerythritol. It is advisable that no more than 1 mol% of the ramifying agents be used in relation to the acid component.

Particularly preferable are polyalkylene terephthalate A made only of terephthalic acid or its reactive derivatives (e.g., the dialkyl esters) and ethylene glycol or 1,4-butanediol.

The polyethylene terephthalates preferably used as component A generally possess an intrinsic viscosity of 0.4 to 1.5 dl/g, preferably 0.5 to 1.3 dl/g, and most preferably 0.6 to 1.2 dl/g; the polybutylene terephthalate used as component A generally possesses an intrinsic viscosity of 0.7 to 1.6 dl/g, preferably 0.8 to 1.3 dl/g, and most preferably 0.8 to 1.05 dl/g, in each case measured in phenol/o-dichlorobenzene (1:1 parts by weight) at 25°C.

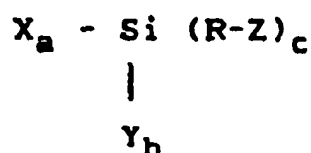
If one wants to use polyethylene terephthalate/polybutylene terephthalate mixtures as polyester component A, then preferably use is made of polyethylene terephthalate with an intrinsic viscosity of 0.65 to 0.9 dl/g; with polybutylene terephthalate with an intrinsic viscosity of 0.8 to 1.4 dl/g and polyethylene terephthalate/polybutylene terephthalate mixing ratios of 90:10 to 10:90, preferably 30:70 to 90:10 (in relation to weight). In place of polyester mixtures, the suitable copolyesters can be used with the same success.

In connection with the ground quartz B, "quartz" does not always mean silicon dioxide; according to the invention, the crystalline  $\alpha$ - and  $\beta$ -quartz silicon dioxide modifications strictly speaking are included by the term "quartz", but it does not designate glassy or amorphous crystalline materials.

The very fine products B are obtained through the grinding of cleaned, if necessary thermally converted quartz and cristobalite sand, e.g., in tube mills, and following particle size cracking, e.g., over winnowing machine, the ground quartz and/or cristobalite consist of at least 99 wt% in reference to at least 99.5 wt% of silicon dioxide. It is - contrary to novaculite - sharp-edged and splinter forming mineralogical material that are crystalline silicon dioxide modifications, but not cryptocrystalline material, e.g., flint, novaculite, and different gemstones; see, for example, Ullmanns Encyclopedia of Technical Chemistry 21 (4<sup>th</sup> Ed.), 440, Verlag Chemie, Weinheim 1982.

Another distinguishing characteristic between quartz and novaculite is that the quartz has a packing density that is twice as high (see Katz and Milewski, Handbook of Fillers and Reinforcements for Plastics, van Nostrand, 1978, pp. 144-154). The quartz that can be used according to the invention preferably possesses a packing density of at least 2.4 kg/dm<sup>3</sup>.

The ground quartz and/or cristobalite B can be used in the smoothed or unsmoothed state; the smoothed state leads to a somewhat higher tenacity; preferred smoothing [agents] are silanes of the formula



where

X is a hydrolyzable group, preferably a C<sub>1</sub>-C<sub>4</sub> alkoxy or H atom,

Y is a hydrogen atom or a monovalent C<sub>1</sub>-C<sub>6</sub>-hydrocarbon residue, preferably vinyl or phenyl,

R is a divalent C<sub>1</sub>-C<sub>20</sub>-hydrocarbon residue, preferably propylene,

Z is a functional group, preferably amino, glycidoxy, or (meth-)acryloyl,

a, c are whole numbers of 1 to 3,

b is zero, 1, or 2,

with:

$$a + b + c = 4$$

preferably a = 3, b = 0, and c = 1.

Preferable silane smoothing agents are e.g.:

$\delta$ -aminopropyltriethoxysilane,  
 $\delta$ -aminopropylphenyldimethoxysilane,  
 $\delta$ -aminopropyltrimethoxysilane,  
 $\delta$ -glycidoxypypyltrimethoxysilane,  
 $\delta$ -methacryloxypropyltrimethoxysilane, or  
 $\delta$ -vinyltrimethoxysilane.

One can add the smoothing agents directly when mixing components A to E; however, it is preferential if this is done during or after grinding of the quartz and/or cristobalite surface area.

As component C, acrylate and butadiene rubbers that can be used are described in the literature; see, e.g., DE-OS 16 94 173, 22 48 242, 23 10 034, 23 57 406, DE-PS 24 44 584 and US-PS 40 22 748, DE-OS 27 26 256 and US-PS 40 96 202, US-PS 38 08 180, EP-A 56 243.

Preferential rubbers C possess a glass transition temperature under  $-30^{\circ}\text{C}$  and include copolymers -- in particular, graft copolymers--with elastic rubber characteristics, and which are produced essentially from at least 2 of the following monomers: 1,3-butadiene, styrene, acrylonitrile, and (meth)-acrylic acid ester with 1 to 18 C atoms in the alcohol component; such polymers are described in "Methods of Organic Chemistry" (Houben-Weyl), Vol. 14/1, Georg Thieme Verlag, Stuttgart, 1961, pp. 393-496 and in C.B. Bucknall, "Toughened Plastics", Appl. Science Publishers, London 1977.

Particularly preferential polymers C are graft polymers.

Preferential graft polymers C possess median particle diameters  $d_{50}$  of 0.05 to 1, preferably 0.1 to 0.8, and in particular 0.2 to 0.6  $\mu\text{m}$ .

The median particle diameter  $d_{50}$  is the diameter above and below which, in each case, 50 wt% of the particles lie. It can be determined by means of ultracentrifuge measurements (W. Scholtan

and H. Lange in *Kolloid. Z und Z polymers* 250 (1972), pp. 782-796) or by means of electron microscopy and joining particle counting (G. Kämpf and H. Schuster, *Angew. Makromolekulare Chemie* 14, (1970), pp. 111-129).

The graft polymers C are crosslinked and have gel contents of at least 50 wt%, preferably at least 80 wt%, and in particular of at least 90 wt%, in relation to graft polymer C.

The gel content of the crosslinked rubbers is determined at 25°C in toluene, the gel content of the crosslinked acryl rubber is determined at 25°C in dimethylformamide (M. Hoffmann, H. Krömer, and R. Kuhn, *Polymeranalytik I and II*, Georg Thieme Verlag, Stuttgart, 1977).

Preferential graft polymers C are graft polymers containing 15 to 60 wt%, preferably 20 to 50 wt%, and in particular 25 to 40 wt% of at least a vinyl or vinylidene monomer chosen from the group consisting of styrene,  $\alpha$ -methylstyrene, acrylonitrile, C<sub>1</sub>-C<sub>8</sub> alkyl acrylates, C<sub>1</sub>-C<sub>8</sub> alkyl methacrylates, hydroxy-C<sub>2</sub>-C<sub>8</sub>-alkyl-(meth)acrylates, and epoxy-C<sub>2</sub>-C<sub>8</sub>-alkyl(meth)acrylates along with 40 to 85 wt%, preferably 50 to 80 wt%, and most preferably 60 to 75 wt%, in each case in relation to graft polymer C, of particle-form crosslinked diene or acrylate rubber.

Preferential graft monomers are methyl methacrylate as well as mixtures made of styrene and methyl methacrylate and mixtures made of styrene and acrylonitrile.

Preferential rubbers are crosslinked homopolymers and/or copolymers made from conjugated C<sub>4</sub>-C<sub>6</sub> dienes, more preferably 1,3-butadiene; the copolymers used can also contain up to 30 wt%, in relation to the [overall] copolymer, of residues of other ethylenically unsaturated monomers, e.g., styrene, acrylonitrile, and acryl or methacrylic acid esters with monovalent C<sub>1</sub>-C<sub>4</sub> alcohols, e.g., methyl acrylate, ethyl acrylate, methyl methacrylate, and ethyl methacrylate.

The production of the rubber graft base and the graft polymers made of it is described, e.g., in "Methods of Organic Chemistry" (Houben-Weyl), Vol. 14/1, Georg Thieme Verlag, Stuttgart, 1961, pp. 393-406, as well as in Ullmanns Encyclopedia of Technical Chemistry, 4<sup>th</sup> edition, Vol. 19, Verlag Chemie, Weinheim, 1981, pages 279 to 284.



Preferential graft bases formed from acrylate rubber are polymers obtained by the polymerization of C<sub>1</sub>-C<sub>8</sub> alkyl acrylates. The polymers can also be copolymers of acrylic acid esters with up to 40 wt%, in relation to the copolymer, of other vinyl monomers such as styrene, acrylonitrile, methyl methacrylate, vinyl esters, and vinyl ethers.

The acrylate rubbers are crosslinked.

Preferential examples of crosslinked monomers with more than one copolymerizing double bond are esters of unsaturated C<sub>3</sub>-C<sub>12</sub> monocarboxylic acids and unsaturated monovalent C<sub>2</sub>-C<sub>12</sub> alcohols or saturated C<sub>2</sub>-C<sub>20</sub> polyols with 2 to 4 OH groups, such as multiple unsaturated heterocyclic compounds, trivinyl isocyanurate, and triallyl cyanurate; in particular, triallyl cyanurate polyfunctional vinyl compounds such as di- and trivinylbenzene as well as triallyl phosphate.

Preferential crosslinked monomers are allyl methacrylate, ethylene glycol dimethacrylate, diallyl phthalate, and heterocyclic compounds that contain at least three copolymerizable ethylenically unsaturated double bonds.

Particularly preferential crosslinked monomers are cyclic monomers such as triallyl cyanurate, triallyl isocyanurate, trivinyl cyanurate, Tris-acryloylhexahydro-sec-triazine, and triallylbenzene.

The amount of crosslinked monomers is preferably 0.02 to 5 wt%, in particular 0.05 to 2 wt%, in relation to the rubber graft [polymer] base.

With cyclic, crosslinked monomers containing at least three ethylenically unsaturated double bonds, it is favorable that no more than 1 wt% be used in relation to the rubber graft [polymer] base.

The mixtures according to the invention can contain glass fibers D, thus the notch impact resistance becomes higher; with an increasing glass fiber content, however, the specific benefits of mineral-filled polyesters, such as surface gloss and distortion property, are not as pronounced.

Examples of the usual auxiliary materials E are nucleating agents and forming agents, providing stability against thermal and UV energy, pigments, dyes, etc.

Mixing the components can be accomplished with ordinary synthetic treating devices such as kneading machines or screw-type extruding machines. One will select the mixing conditions in such a way that the viscosity of the polymer components does not drop or hardly does not drop. Also, pre-mixing of the individual components can be performed.

Another subject of the invention is thus a technique for the production of the mixtures according to the invention, performed by mixing the components, preferably at temperatures of 250 to 320°C.

The production of molded articles by means of injection molding is known (e.g. E. J. Rubin, Injection Molding Theory and Practice, Wiley Interscience, 1972); suitable mass temperatures are about 250 to 270°C, preferably implementation temperatures of 80 to 130°C.

Another item is thus the use of the mixtures according to the invention for the production of molded articles, preferably by injection molding,

From the mixtures according to the invention, the most diverse items, e.g. carburetor parts, distributors, electrical components, housing parts, ventilation screens, and lamp-sockets, can be made.

### **Examples and Comparative Tests**

Polybutylene terephthalate with an intrinsic viscosity of 0.93 dl/g and polyethylene terephthalate with an intrinsic viscosity of 0.77 dl/g in the weight ratio of 60:40 were mixed and crosslinked by compounding on a double-axe extruder with small amounts of stabilizer, parting agent, and crystallization accelerator as well as the indicated amounts of different inorganic additives shown in Tables 1 and 2. Additionally, test data related to the molding materials of the produced test

specimens are shown. The superiority of the systems with ground quartz and cristobalite is evident.

Table 1

	Type of mineral	Amount (wt%, based on the total mixture)	Shock resistance (DIN 53453) [kJ/m <sup>2</sup> ]	Notch impact resistance (DIN 53453) [kJ/m <sup>2</sup> ]	Tension force modulus (DIN 53455) [MPa]	Vicat B (DIN 53460) [°C]	Bending modulus (DIN 53452) [MPa]
1	Non-smooth quartz powder, particle diameter: ≥ 50 % are <2.5 μm	20	>100	1.6	3810	171	3440
2	With epoxysilane smooth quartz powder; particle diameter: ≥70% are <2.5 μm	40	83	1.6	5650	193	4860
3	With aminosilane smooth quartz powder; particle diameter: ≥70% are <2.5 μm	40	>100	1.6	5710	191	4900
4	With aminosilane smooth quartz powder; particle diameter: ≥70% are <2.5 μm	40	92	1.6	5770	193	5050
5	With epoxysilane smooth ciatobalite powder; particle diameter: ≥65% are <2.5 μm	40	90	1.6	5900	191	5180

Table 2

Type of mineral testing		Amount (wt%, based on total mixture)	Shock resistance (DIN 53453) [kJ/m <sup>2</sup> ]	Notch impact resistance (DIN 53453) [kJ/m <sup>2</sup> ]	Tension force modulus (DIN 53455) [MPa]	Vicat B (DIN 53460) [°C]	Bending modulus (DIN 53452) [MPa]
A	Aminosilane-treated calcined kaolin	20	91	1.5	3960	182	3560
B	Particle size: 50% ≤ 2 µm	40	33	1.5	6630	198	5800
C	Epoxysilane-treated wallastonite, particle diameter : 63% ≤ 2.5 µm	40	41	1.6	5870	186	5190
D	Untreated talcum powder particle size: 69% ≤ 2 µm	40	14	138	8880	191	8690
E	Untreated novaculite particle size: 80% < 5 µm Particle diameter TG: 2.7 µm	30	15	6.1	4890	178	4240
F	Untreated novaculite particle size: 100% < 5 µm Durch Particle diameter TG: 2.7 µm	30	61	2.3	5010	183	4240

**Patent claims:**

## 1. Mixtures made from:

- A) 20 to 80 wt% of thermoplastic polyester,
- B) 5 to 50 wt% of a mineral filling material,
- C) 0 to 30 wt% of an acrylate or butadiene rubber,
- D) 0 to 30 wt% of glass fibers, and
- E) 0 to 10 wt% of ordinary auxiliary materials,

whereby the percentage figures refer to the sum of components A to E,

characterized by the fact that the filling material B is ground quartz and/or ground cristobalite, of which at least 50 wt% possess a particle diameter of 2.5  $\mu\text{m}$  at the most.

2. Mixtures according to Claim 1, characterized by the fact that they contain 40 to 75 wt% of component A.

3. Mixtures according to Claims 1 and 2, characterized by the fact that they contain 20 to 50 wt% of component A.

4. Mixtures according to Claims 1-3, characterized by the fact that they contain 10 to 25 wt% of component C,

5. Mixtures according to Claims 1-4, characterized by the fact that the thermoplastic polyester is chosen from the group consisting of polyethylene terephthalate, polybutylene terephthalate, their mixtures, and poly(ethylene/butylene terephthalate).

6. Technique for the production of the mixtures according to Claims 1 to 5 by mixing the components at temperatures of 250 to 320°C.
7. Use of the mixtures according to Claims 1-5 for the production of molded articles.



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# EUROPEAN SEARCH REPORT

## 0221338

Application Number  
EP 86 11 3390

RELEVANT DOCUMENTS			
Category	Marking of the document with indication, to the extent necessary, the relevant parts	Requirement Concerns	CLASSIFICATION OF THE APPLICATION (INT. CL.6)
D,X	US-A-4 018,738 (H.L.RAWLINGS) * Patent claims 1-12; Column 3, lines 7-40 *	1-7	C08L 67/02 C08K 3/36
X	--- CHEMICAL ABSTRACTS, tape 85, NR. 18, November 1976, page 55, summary No. 125139p, Columbus, Ohio, US; & JP-A-76 81,849 (TEIJIN) 17 July 1976 * Altogether *	1-7	
A	--- PATENT ABSTRACTS OF JAPAN, tape 7, NR. 108 (C-165)[1253 ], 11 May 1983; & JP-A-58 29,858 (NITTO DENKI) 22-02-1983	1	
A	--- RUBBER, ASBESTOS, SYNTHETICS, tape 36, NR. 12, December 1983, pages 658-667, A.W.Guntner publishing house, Stuttgart, DE; D.SKUDELNY aluminum et: " mineral filling materials from quartz, Cristobalite and quartz property " * Page 658, paragraph 3.3; Page 663, paragraph 4 - page 664 *	1	INVESTIGATED SUBJECTS (INT. CL.6) C08L C08K
D,A	--- EP-A-0 056,243 (BAVARIAN) * Patent claims 1-12; Page 7, lines 1-8 *	1-7	
The available search report was provided for all patent claims			
Place of Search The Hague		Conclusion Date of the Search January 15, 1987	Examiner DECOCKER L.
CATEGORY OF THE DOCUMENTS MENTIONED X: of special importance alone regards Y: of special importance in connection with another publication of the same category A: technological background O: not-written revealing P: Intermediate literature		T: the invention at the basis lying theories or principles E: older patent document, which was however only published at or after the date of application D: in the application stated document ..... &: Member the same patent family, agreeing document	



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